Supplementary Material (ESI) for Chemical Communications

SUPPORTIING INFORMATION

Preferential Suppression of High-Energy Upconverted Emissions of Tm^{3+} by Dy^{3+} ions in $Tm^{3+}/Dy^{3+}/Yb^{3+}$-doped $LiYF_4$ Colloidal Nanocrystals

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Summary:

1) Experimental Details

The Tm^{3+}/ Yb^{3+}/ Dy^{3+}-doped $LiYF_4$ colloidal nanocrystals (with 0.5% Tm; 15% Yb; and 0.1% or 0.075% Dy) were prepared by the thermal decomposition method reported earlier[1]. Briefly, the lanthanide (Y^{3+}, Tm^{3+}, Yb^{3+} and Dy^{3+}), trifluoroacetates were prepared by reacting stoichiometric quantities of Y_2O_3, Tm_2O_3, Yb_2O_3 and Dy_2O_3, in CF_3COOH/H_2O (50:50 v/v) and heating the corresponding mixture to reflux at 80 °C. Once the precursor solution became clear, it was allowed to dry at 60 °C and the corresponding lanthanide trifluoroacetate precursors were mixed with CF_3COOLi, oleic acid (20 mL), and 1-octadecene (20 mL) and degassed by heating to 110 °C under vacuum with constant stirring. After 30 min, the temperature of the mixture was increased to 330 °C at a rate of 5 °C min^{-1} under an Ar flow. The mixture was held at this final temperature for 1 h after which it was allowed to cool to 70 °C prior to precipitation with absolute ethanol. The nanocrystals were then separated by centrifugation and further purified by dispersing them in hexane followed by precipitation with ethanol.

The XRD pattern was collected using the Rigaku SmartLab X-ray spectrometer attached with D/tex ultra detector and Cu K_α source operating at 50 mA and 40 kV. Scan range was set from 10-70° 2θ with a step size of 0.02° and a count time of 2 sec.

TEM analysis of the colloidal dispersion of nanocrystals was performed using a Philips CM200 microscope operating at 200 kV equipped with a charge-coupled device (CCD) camera (Gatan). Prior to analysis, a 10 mg sample was dispersed in 10 g of toluene to yield an approximate 0.1 wt% solution. A drop of the resulting solution was evaporated on a formvar/carbon film supported on a 300 mesh copper grid (3 mm in diameter).

The upconversion emission spectra were obtained using a Coherent fiber-coupled F6 series 978 nm laser diode (maximum power of 800 mW), coupled to a 100 μm (core) fiber. For the upconversion

[1] V. Mahalingam, F. Vetrone, R. Naccache, A. Speghini and J. A. Capobianco. *J. Mater. Chem.*, 2009, **19**, 3149; J.-C. Boyer, F. Vetrone, L. A. Cuccia and J. A Capobianco, *J. Am. Chem. Soc.*, 2006, **128**, 7444.

studies, the nanocrystal samples (1 wt % in toluene) were placed in 1 cm path-length quartz cuvettes (Hellma, QS). The upconverted emissions were collected at right angle with respect to the incident beam and subsequently dispersed by a 1 m Jarrell-Ash Czerny-Turner double monochromator with an optical resolution of ~0.25 nm. The visible emissions were detected by a thermoelectrically cooled Hamamatsu R943-02 photomultiplier tube. A preamplifier model SR440 Standard Research Systems, processed the photomultiplier signals and a gated photon counter model SR400 Standard Research Systems data acquisition system was used as an interface between the computer and the spectroscopic hardware. The signal was recorded under computer control using the Standard Research Systems SR465 software data acquisition/analyzer system. The ultraviolet emissions were collected with a Spex Minimate 1/4 m monochromator and detected with an Oriel 70680 photomultiplier tube. It should be noted that although, the UV emissions are measured with a different detector, it is found by measuring the blue emissions under the same conditions that both UV emissions are quite intense compared to the blue emissions. For the lifetime measurements, the sample was excited at 355 nm using a 60 W pulsed Xe microsecond flash lamp from the Edinburg instruments and the photons were collected using the PMT.

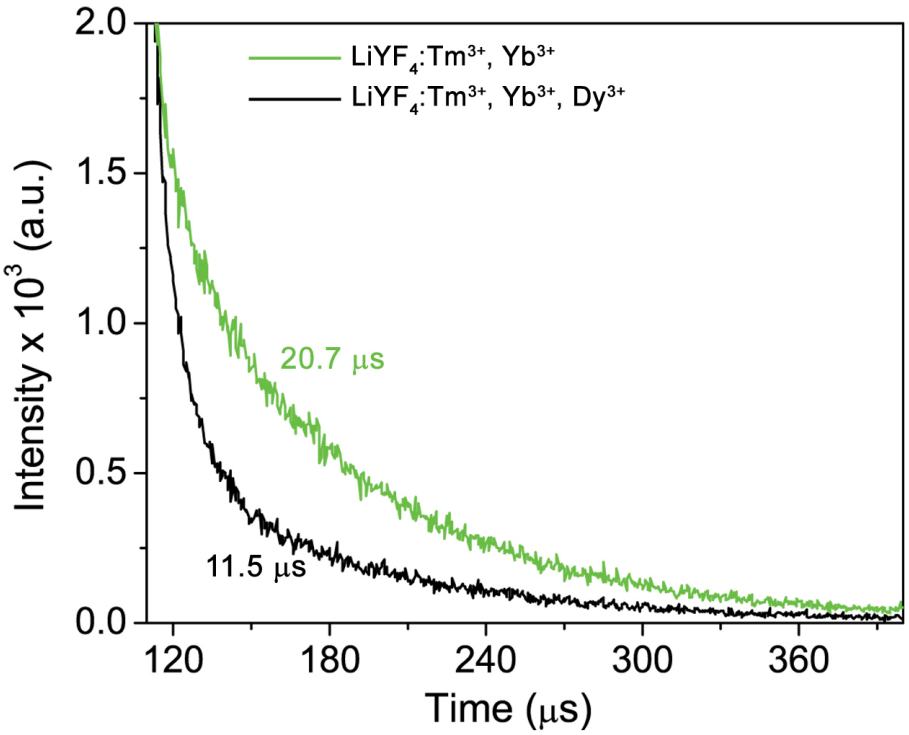

Fig S1. Decay curves indicating a reduction in the lifetime of the $^1D_2$ state of the Tm^{3+} for the $Tm^{3+}/Dy^{3+}/Yb^{3+}$ -doped $LiYF_4$ nanocrystals with respect to the $LiYF_4$ nanocrystals without Dy^{3+} ions.